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Charge Transfer, Double and Bond-Breaking Excitations with Time-Dependent Density Matrix Functional Theory

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Time-dependent density functional theory (TDDFT) in its current adiabatic implementations exhibits three remarkable failures: (a) completely wrong behavior of the excited state surface along a bond-breaking coordinate; (b) lack of doubly excited configurations; (c) much too low charge transfer excitation energies. These TDDFT failure cases are all strikingly exhibited by prototype two-electron systems such as dissociating H_2 and HeH^+ . We find for these systems with time-dependent density *matrix* functional theory that: (a) Within previously formulated simple adiabatic approximations, the bonding-to-antibonding excited state surface as well as charge transfer excitations are described without problems, but not the double excitations; (b) An adiabatic approximation is formulated in which also the double excitations are fully accounted for.

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Dissociation of molecular systems poses a serious challenge within the DFT framework. This is already true for the ground state energy curve cf., e.g., Ref. [1]. For excited states, the problems are even worse; there are various kinds of excitations which are not correctly represented in TDDFT calculations. Figure 1(a) displays the failure of TDDFT (in its adiabatic BP86 variant) for the potential energy surface (PES) of the first excited state of H_2 , $1^1\Sigma_u^+$, corresponding to the $\sigma_g \rightarrow \sigma_u$ orbital excitation. As highlighted in Ref. [2], this PES goes to zero instead of going asymptotically to ca. 10 eV. B3LYP does not improve the situation at all. In Fig. 1(b), we document the TDDFT problem with double excitations for the Σ_g^+ excitation energies of dissociating H_2 . It is evident that there is an exact state (the third at $R_e = 1.4$ Bohr) which is missing in the TDDFT calculations. This is the doubly excited $(\sigma_g)^2 \rightarrow (\sigma_u)^2$ state. The double-excitation nature is indicated with dots on the PES curve, and it is clear that, in the accurate calculations, the doubly excited state becomes lower with increasing R and has avoided crossings with the second and first state, becoming the lowest excited $1^1\Sigma_g^+$ state ($2^1\Sigma_g^+$) from ca. 2.5 Bohr onwards. This state is completely missing in the TDDFT calculations. After some initial optimism that such doubly excited states would be accurately calculated in TDDFT, it has become clear this is not the case [3–5]. Figure 1(c) gives an example of the charge transfer problem. The excitation energies of HeH^+ are shown along the dissociation coordinate for the lowest three $1^1\Sigma$ excited states. At long distance, these excitations have strong charge transfer character, from $\text{He}(1s)$ to $\text{H}(1s)$ in $2^1\Sigma$ and from $\text{He}(1s)$ to $\text{H}(2s, 2p_z)$ in $3^1\Sigma$ and $4^1\Sigma$. The TDDFT excitation energies exhibit at long distance the well-known severe underestimation of charge transfer excitations [6]. The hybrid functional B3LYP improves somewhat on the pure GGA BP86. We note that the excited state energy does not have a $1/R$ asymptotic behavior for this type of charge transfer

excited state, the fragments being He^+ and neutral H. The quoted problems are caused by fundamental flaws in the adiabatic f_{xc} , not in a deficient v_{xc} .

A remedy for these deficiencies of time-dependent density functional theory might be sought in density *matrix* functional theory (DMFT) [7–10,10–13]. For the ground state total energy curve along the dissociation coordinate, successes have already been reported [12] with approximate DM functionals that represent improvements on the forms formulated long ago by Müller [7] and Buijse and Baerends [8,9]. It is the purpose of the present Letter to address the above-mentioned problem cases for TDDFT excitation energy calculation with DMFT, using a further development of linear response based time-dependent density matrix functional theory [14,15]. We will restrict ourselves to the two-electron systems H_2 and HeH^+ , which exhibit all the problems, but which have the advantage that we do not have to introduce an approximate functional since the exact one is known for two-electron systems. The spatial part of a singlet two-electron wave function is symmetric at all times t , so the matrix $C(t)$ of expansion coefficients in a two-electron product basis $\chi_p(\mathbf{r})\chi_q(\mathbf{r}')$ is symmetric and can be diagonalized at each t , as originally noted by Löwdin and Shull [16] for the wave function $\Psi(\mathbf{r}, \mathbf{r}'; t)$,

$$\Psi = \sum_{pq} C_{pq}(t) \chi_p(\mathbf{r}) \chi_q(\mathbf{r}') = \sum_{\mu} c_{\mu}(t) \phi_{\mu}(\mathbf{r}t) \phi_{\mu}(\mathbf{r}'t).$$

The orbitals $\{\phi_{\mu}\}$ are time-dependent, since the wave function will have a different spectral representation at different times. To distinguish this special time-dependent basis $\{\phi_{\mu}(t)\}$ from the stationary one, $\{\chi_p\}$, we use Greek letters as indices for the time-dependent basis and Latin for the time-independent functions. The one-particle density matrix $\gamma(\mathbf{r}, \mathbf{r}'; t)$ can be written

$$\gamma = \sum_{pq} \gamma_{pq}(t) \chi_p(\mathbf{r}) \chi_q^*(\mathbf{r}') = \sum_{\mu} n_{\mu}(t) \phi_{\mu}(\mathbf{r}t) \phi_{\mu}^*(\mathbf{r}'t)$$

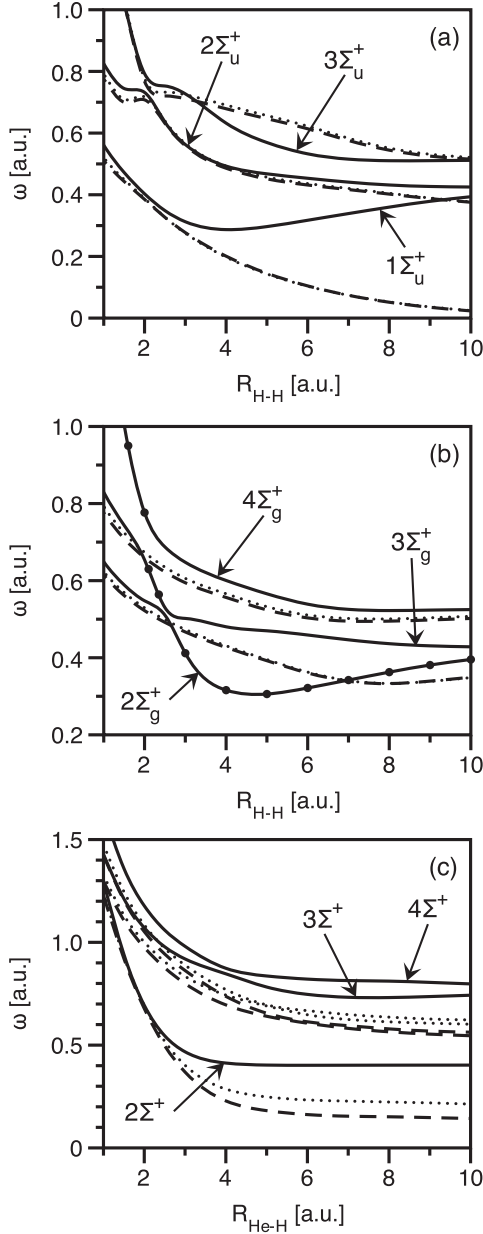


FIG. 1. Σ_u^+ (a) and Σ_g^+ (b) TDDFT excitation energies for H_2 and Σ^+ TDDFT excitation energies for HeH^+ (c). Solid lines: exact in cc-pVTZ basis; dashed lines: TDDFT-BP86; dotted lines: TDDFT-B3LYP.

which shows the $\{\phi_\mu(t)\}$ are the time-dependent NOs and the wave function coefficients $c_\mu(t)$ are related to the NO occupation numbers, $n_\mu(t) = 2|c_\mu(t)|^2$. The two-matrix reduces to the particularly simple form

$$\begin{aligned} \Gamma(\mathbf{r}_1\mathbf{r}_2, \mathbf{r}'_1\mathbf{r}'_2; t) &= \sum_{pqrs} \Gamma_{pqrs}(t) \chi_s^*(\mathbf{r}'_1) \chi_r^*(\mathbf{r}'_2) \chi_q(\mathbf{r}_2) \chi_p(\mathbf{r}_1) \\ &= \sum_{\mu\nu\rho\sigma} [2c_\mu(t)c_\sigma^*(t)\delta_{\mu\nu}\delta_{\sigma\tau}] \phi_\sigma^*(\mathbf{r}'_1t) \phi_\rho^*(\mathbf{r}'_2t) \\ &\quad \times \phi_\nu(\mathbf{r}_2t) \phi_\mu(\mathbf{r}_1t). \end{aligned}$$

This shows that in a singlet two-electron system the two-matrix can be reconstructed easily from the one matrix. It is this property which gives two-electron systems their special place in DMFT. The electron-electron interaction energy $W(t) = \langle \Psi(t) | \hat{W} | \Psi(t) \rangle$ can be written in terms of the matrix \mathbf{W} with elements $W_{\mu\nu}(t)$

$$W_{\mu\nu} = \sum_{\rho\sigma\tau} \Gamma_{\mu\rho\sigma\tau}(t) w_{\tau\sigma\rho\nu}(t) = 2 \sum_{\sigma} c_\sigma^*(t) c_\mu(t) w_{\sigma\sigma\mu\nu}(t)$$

$$w_{\tau\sigma\rho\nu} = \int d\mathbf{r}_1 \int d\mathbf{r}_2 \phi_\tau^*(\mathbf{r}_1t) \phi_\sigma^*(\mathbf{r}_2t) r_{12}^{-1} \phi_\rho(\mathbf{r}_2t) \phi_\nu(\mathbf{r}_1t)$$

as $W(t) = \frac{1}{2} \text{Tr}\{\mathbf{W}\}$. Note that the two-electron integrals are related to the ones in conventional notation as $w_{pqrs} = \langle pq | sr \rangle$. The equation of motion of the one-matrix can now be written in the form that was derived in [14] and used in [15]

$$\begin{aligned} i\dot{\gamma}_{kl}(t) &= \sum_s [h_{ks}(t)\gamma_{sl}(t) - \gamma_{ks}(t)h_{sl}(t)] \\ &\quad + [W_{kl}^\dagger(t) - W_{kl}(t)], \end{aligned} \quad (1)$$

where h_{ks} , h_{sl} are matrix elements of the one-electron part of the Hamiltonian (kinetic energy and nuclear field) and $W_{kl}(t)$ is defined as the contraction of the two-matrix in the stationary basis with the two-electron integrals in the same basis, $W_{kl}(t) = \sum_{rst} \Gamma_{krst}(t) w_{lsrl}(t)$. The simplifications afforded by the simple representation of the one-matrix and two-matrix in terms of the diagonal wave function coefficients $\{c_\mu(t)\}$, can now be exploited to derive (with some algebra, see Ref. [17]) exact equations for the excitation energies. To this end, Eq. (1) is first written in linear response form. Upon application of a small perturbing external potential $\delta v(\mathbf{r}, t)$ using the NOs at $t = 0$ as the stationary basis $\{\chi\}$, one obtains to first order

$$\begin{aligned} i\partial_t \delta\gamma_{kl}(t) &= \sum_r [\delta v_{kr}(t)\gamma_{rl} - \gamma_{kr}\delta v_{rl}(t)] \\ &\quad + \sum_r (h_{kr}\delta\gamma_{rl}(t) - \delta\gamma_{kr}(t)h_{rl}) \\ &\quad + [\delta W_{kl}^\dagger(t) - \delta W_{kl}(t)]. \end{aligned} \quad (2)$$

Since γ is Hermitian, the degrees of freedom are the real and imaginary parts of the lower triangle off-diagonal matrix elements $\delta\gamma_{kl}$, $l < k$, and the real diagonal elements $\delta\gamma_{kk} = \delta n_k$. In order to obtain a symmetric matrix problem, we work in practice with the related quantities:

$$\delta\tilde{\gamma}_{kl}^{R/I}(\omega) \equiv \frac{\delta\gamma_{kl}^{R/I}(\omega)}{2(c_l \pm c_k)} \quad (3)$$

$[c_l = c_\lambda(0)]$ and define the matrices

$$\begin{aligned} A_{kl, sr} &\equiv (\delta_{kr}\delta_{ls} + \delta_{ks}\delta_{lr})E_0 - (w_{kl sr} + w_{kl rs}) \\ &\quad - (\delta_{kr}h_{ls} + \delta_{ks}h_{lr} + \delta_{lr}h_{ks} + \delta_{ls}h_{kr}) \end{aligned} \quad (4a)$$

$$C_{kl, r} \equiv A_{kl, rr} \quad E_{k, r} \equiv A_{kk, rr} \quad (4b)$$

where E_0 is the energy of the ground state. Note that A is Hermitian, and C and E are just submatrices of A .

We then obtain the equations

$$\begin{pmatrix} \frac{CC^T}{\omega} & -A & \frac{CE}{\omega} \\ -A & 0 & -C \\ \frac{EC^T}{\omega} & -C^T & \frac{E^2}{\omega} \end{pmatrix} \begin{pmatrix} \delta\tilde{\gamma}^R(\omega) \\ \delta\tilde{\gamma}^I(\omega) \\ \delta\tilde{n}(\omega) \end{pmatrix} = \omega \begin{pmatrix} \delta\tilde{\gamma}^R(\omega) \\ \delta\tilde{\gamma}^I(\omega) \\ \delta\tilde{n}(\omega) \end{pmatrix}. \quad (5)$$

The ω values for which this system gives nontrivial solutions represent excitation energies. Beyond the linear response approach, no approximations have yet been introduced, and from these exact TDDMFT equations indeed the exact excitation energies are found, equal to those from a full CI calculation in the same basis set. This includes the double excitations. It is interesting to observe that the dimension of the matrix problem (5) is smaller than the full CI problem, and indeed it is the ω -dependence of the matrix which causes the appearance of additional roots. The exact TDDMFT matrix illustrates how ω -dependence of the exchange-correlation kernel enters into the response equations [3,4].

For practical applications, in particular, also for systems with more than two electrons, we need adiabatic approximations, which yield an ω -independent matrix so that simple diagonalization will yield the excitation energies. The $\omega \rightarrow 0$ limit of the exact TDDMFT matrix of Eq. (5) is relevant for the static limit of frequency dependent polarizability calculations. It is, however, immediately clear that the $1/\omega$ terms in the exact Eq. (5) will diverge for small ω . Not surprisingly, the so-called static approximation (SA) introduced in Ref. [14] yields a matrix in which those terms no longer appear:

$$\begin{pmatrix} 0 & -A & 0 \\ -A & 0 & -C \\ 0 & -C^T & 0 \end{pmatrix} \begin{pmatrix} \delta\tilde{\gamma}^R(\omega) \\ \delta\tilde{\gamma}^I(\omega) \\ \delta\tilde{n}(\omega) \end{pmatrix} = \omega \begin{pmatrix} \delta\tilde{\gamma}^R(\omega) \\ \delta\tilde{\gamma}^I(\omega) \\ \delta\tilde{n}(\omega) \end{pmatrix}. \quad (6)$$

Unfortunately, the SA approximation turns out to be deficient in the sense that it yields m excitation energies equal to zero (m is the size of the basis set). Further analysis reveals that these spurious zeros arise from failure to include properly the doubly excited states $(\chi_1)^2 \rightarrow (\chi_p)^2$ (there are m diagonal excitations $(\psi_1)^2 \rightarrow (\psi_i)^2$, $i = 1 \dots m$; ψ_1 is the occupied $1\sigma_g$ or 1σ orbital in our systems). This will be clear from the examples below. In an attempt to improve upon the SA, the so-called AA has been proposed [15]. Here the third set of SA equations [those arising from the bottom row of the partitioned matrix of Eq. (6)], are replaced by the static perturbation equation for the energy change under a (static) potential perturbation,

$$C^T \delta\tilde{\gamma}^R(0) + E \delta\tilde{n}(0) - \delta\tilde{v}^D(0) = -c \delta E(0). \quad (7)$$

This approximation, which we will call AA1, proves to fail again with the double excitations [17]. We propose an

adiabatic approximation in which the static perturbation Eqn. (7) does not replace, but is incorporated into the third set of the Eqn. (6). Some of the ω dependence is retained and the double excitations which are represented by the $\delta\tilde{n}$ vector are included via the $\omega \delta\tilde{n}$ term. In the $\omega \rightarrow 0$ limit, the equations still reduce, as required, to the static perturbation equation. In that way, the full set of equations becomes consistent because imposing Eqn. (7) is actually a requirement for the elimination of the $1/\omega$ terms in the first two sets of equations. We thus obtain the AA2 set of equations

$$\begin{pmatrix} 0 & -A & 0 \\ -A & 0 & -C \\ C^T & -C^T & E \end{pmatrix} \begin{pmatrix} \delta\tilde{\gamma}^R(\omega) \\ \delta\tilde{\gamma}^I(\omega) \\ \delta\tilde{n}(\omega) \end{pmatrix} = \omega \begin{pmatrix} \delta\tilde{\gamma}^R(\omega) \\ \delta\tilde{\gamma}^I(\omega) \\ \delta\tilde{n}(\omega) \end{pmatrix}. \quad (8)$$

Unfortunately, these equations have the deficiency that some of the negative ω eigenvalues are not equal to the corresponding positive ones. But they do properly include the double excitations, and the positive eigenvalues, which we identify with the excitation energies, are remarkably accurate (even exact, see below). We compare in Fig. 2(a) the various adiabatic TDDMFT excitation energies with the exact ones for the Σ_u^+ excited states. Interestingly, in this symmetry, the SA, AA1, and AA2 all coincide with the exact excitation energies along the whole binding distance. This is related to the symmetry: we find that for different symmetries than the ground state, all adiabatic approximations yield perfect excitation energies. This also holds for the Π_u and Π_g excited states. The significant observation, however, is that the adiabatic TDDMFT, in contrast to adiabatic TDDFT, has no problem with the $\sigma_g \rightarrow \sigma_u$ excitation along the whole bond-breaking coordinate.

Results for the Σ_g^+ excitations are shown in Fig. 2(b). Now the adiabatic approximations are not identical to the exact ones. However, the performance of the adiabatic approximations SA and AA1 is rather good, except for the fact that they are completely missing the state with predominantly doubly excited character, that is high lying at short distance and then on its way down crosses the other states (see again the dots indicating the doubly excited electronic character on the different curves). This deficiency of the SA and AA1 adiabatic approximations in TDDMFT is actually very similar to the adiabatic TDDFT deficiency noted in the beginning. On the other hand, the AA2 approximation coincides with the exact results. It brings in the coupling to the diagonal doubles very effectively, in fact, perfectly.

Finally, the HeH^+ excitations in the Σ^+ symmetry are shown in Fig. 2(c). The low lying Σ^+ excitations are, similar to the Σ_g^+ excitations in H_2 , not perfect in the SA and AA1 approximations, but they are clearly rather accurate. In this case, the AA1 performs better than the SA, especially for the lowest Σ^+ excitation and also for the other two. The AA2 is exact for all the Σ (and Π , not shown) excited states. The important point is that at long

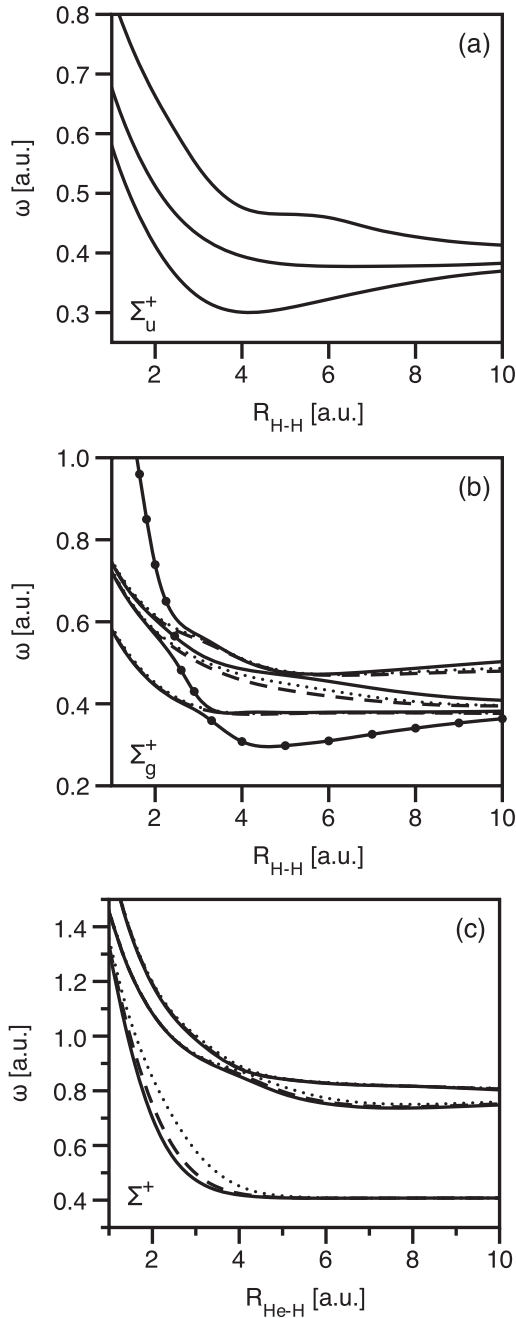


FIG. 2. Σ_u^+ (a) and Σ_g^+ (b) excitations for H_2 and Σ^+ excitations for HeH^+ (c). Solid lines: exact and the positive roots of AA2; dotted lines: SA; dashed lines: AA1.

distance, the lowest excited state, $2\Sigma^+$ at ca. 0.40 a.u., is a pure CT state, $He(1s) \rightarrow H(1s)$. The $3\Sigma^+$ at ca. 0.74 a.u. is at long distance a mixed local [$He(1s) \rightarrow He(2s)$] and charge transfer [$He(1s) \rightarrow H(2s, 2p)$] excitation. The $4\Sigma^+$ at ca. 0.82 a.u. is mostly CT, $He(1s) \rightarrow H(2s, 2p)$. All of the pure and mixed CT excitations are represented

accurately in all adiabatic TDDMFT calculations, even exactly with AA2.

We conclude that the well-known failure cases of adiabatic TDDFT can in principle be solved without difficulty in adiabatic TDDMFT. Whether adiabatic TDDMFT will prove to be widely applicable in N -electron systems with $N > 2$, will crucially depend on the quality of the approximate density matrix functionals that are needed in those cases. Good progress is being made with such functionals for the ground state, both at equilibrium geometry [13] and along the dissociation coordinate [12], which offers good prospects for the response calculations. We note that TDDMFT does not rely on a zero-order approximation of excitation energies as orbital energy differences, like the virtual minus occupied Kohn-Sham orbital energy differences in TDDFT. This may sometimes be an advantage for TDDMFT; e.g., it is the “wrong” orbital energy difference in the case of CT excitations that is the main cause of the trouble for TDDFT. On the other hand, this lack of an “easy” zero-order starting point may put higher demands on the NO functionals in the TDDMFT case. Work on the general N -electron case is in progress.

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